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LIGAND EXCHANGE REACTIONS IN ORGANOMETALLIC VAPOR-PHASE
EPITAXY

by

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Ligand Exchange Reactions in Organometallic Vapor-Phase Epitaxy

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The organometallic vapor-phase epitaxy (OMVPE) of CdZnTe and InGaAs alloys has been studied using on-line infrared spectroscopy and ex-situ X-ray crystallography. During II-VI OMVPE, ligand exchange reactions between dimethylcadmium and diethylzinc produce more reactive ethylcadmium species, and less reactive methylzinc species. During III-V OMVPE, reactions between trimethylindium and triethylgallium produce more reactive ethylindium compounds and less reactive methylgallium compounds. The large difference in reactivities of these sources makes it difficult to control the group II and III composition during CdZnTe and InGaAs OMVPE.

Key words: CdZnTe, InGaAs, organometallic vapor-phase epitaxy (OMVPE), alkyl ligand exchange reactions, infrared spectroscopy (IR), X-ray diffraction (XRD)

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INTRODUCTION

The fabrication of large area infrared focal plane arrays (IRFPAs) requires the deposition of HgCdTe photodiodes directly on Si or GaAs readout chips.^{1,2} The HgCdTe can be exactly lattice matched to a buffer layer of CdZnTe containing 4% zinc. It is essential that the CdZnTe layer is highly uniform in composition, thickness and crystallinity, as slight variations in the zinc content can seriously impact the quality of the HgCdTe epilayer.

The same argument holds true for the OMVPE of III-V alloys, such as for lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ on InP substrates in the manufacture of heterojunction bipolar transistors (HBTs). The control of the composition becomes even more complicated when one attempts to heavily carbon dope the InGaAs base layer with CCl_4 .³

Recently, we found that exchange reactions occur between the alkyl ligands of dimethylcadmium (DMCd) and diethylzinc (DEZn) in the feed lines on the way to the reactor.⁴ This phenomenon explains the origin of the unusual alloy segregation behavior in CdZnTe OMVPE.^{5,6} Ligand exchange reactions between trimethylamine alane and trimethylgallium precursors were observed during AlGaAs MOVPE, leading to growth of non-uniform layers.⁷ It can be expected that similar reactions occur during the growth of InGaAs using trimethylindium (TMIn) and triethylgallium (TEGa). In this paper, the effect of ligand exchange reactions between group II sources and between III sources on the composition of the respective alloys will be discussed.

EXPERIMENTAL

The experimental apparatus and procedures used for II-VI OMVPE have been described previously.^{8,9} An atmospheric-pressure OMVPE reactor was used to deposit CdZnTe on the inner walls of a glass reactor tube. The electronic-grade sources, DMCd, DEZn, dimethylzinc (DMZn) and diisopropyltelluride (DIPTe) were vaporized into helium, which were then diluted further with hydrogen and fed to the reactor.

The III-V growth experiments were carried out using a modified Crystal Specialties low-pressure OMVPE reactor at 99 Torr. Electronic-grade TMIn, trimethylgallium (TMGa), TEGa and tertiarybutylarsine (TBAs) were used as the organometallic sources, while palladium-diffused hydrogen was used as the carrier gas.

The consumption rates of the organometallic sources were determined by monitoring the gas-phase composition of the reactor feed and effluent with a BioRad FTS-7 infrared spectrometer. Infrared spectra of the gas streams were collected by passing them through a small flow cell, 17.7 cm long and 3.0 cm in diameter, that was sealed with KBr windows. The intense vibrational bands of the organometallic sources detected between 1600 and 450 cm^{-1} are mostly well resolved from each other, and provide a means of independently monitoring the consumption of each molecule during OMVPE.⁹

The CdZnTe films were analyzed over the length of the reactor tube using a $\theta/2\theta$ scan on a Crystal Logic powder diffractometer. The film thickness in each section of the tube was also determined.

RESULTS AND DISCUSSION

Figure 1 shows the infrared spectra of mixtures of DMCd and DEZn, and those of TMIn and TEGa as a function of the initial feed composition. The frequencies depicted are for the C-H bending modes of the alkyl ligands ($800\text{--}550\text{ cm}^{-1}$) and for the stretching modes of the metal-carbon bonds ($750\text{--}450\text{ cm}^{-1}$).¹⁰⁻¹² In both cases, the infrared spectra of the mixtures, $x=0.3$ and 0.7 , are not a simple weighted summation of the infrared spectra of the pure compounds, $x=0.0$ and 1.0 . Instead, the infrared spectra contain several new absorption bands.

The new bands show similarities with the sources initially fed, suggesting the formation of new organometallic compounds by ligand exchange reactions. Four new organometallic compounds are identified from the reaction between DMCd and DEZn. The IR spectra of these molecules have been extracted from the mixture by subtracting out the bands due to the known compounds, DMCd, DEZn and DMZn. A similar procedure was used to identify five of the six possible ligand exchange products from the reaction of TMIn with TEGa. An infrared spectrum of triethylindium (TEIn) was not observed in the mixtures. The organogallium exchange products were recovered by repeating the measurements with different mixtures of TEGa and TMGa. The infrared spectra of each organometallic compound in the mixture of DMCd and DEZn and of TMIn and TEGa are shown in Fig. 2(a) and (b), respectively.

Ligand exchange between group II and between group III organometallic compounds was investigated during the 1960's.¹³⁻¹⁷ It was found that these reactions proceed rapidly under mild conditions in solution. We assume that the same mechanism and

thermodynamics hold for the reactions in the gas as for those in solution. Recent ^1H -NMR measurements on a 1:1 mixture of DMCd and DEZn in the liquid reveal that within experimental error, the same exchange products are formed at the same relative concentrations as those measured in the gas.¹⁸

The ligand exchange reactions have a profound effect on the composition of the reactor feed, and in turn, the growth kinetics. Figure 3 shows the dependence of the fractional partial pressure of DMCd and DEZn , and TMIn and TEGa on the feed composition x . The curves are concave up because the partial pressures of the precursors in the mixture have decreased compared to those initially in the feed. The decrease in the initial concentration is more severe for DMCd and TMIn than for DEZn and TEGa , as evidenced by the deviations from their respective diagonals. Shown in Tables 1 and 2 are the relative partial pressures of each organometallic compound obtained from the mixtures of DMCd with DEZn , and of TMIn with TEGa , at $x=0.3$ and 0.7 . Inspection of these data reveals that the relative concentrations of the exchange products vary significantly with x . The amount of DMZn produced at $x=0.3$ is more than half of the total concentration of organozinc species, while DMCd and methylethylcadmium (MECd) exist in equal amounts. By contrast, at $x=0.7$, almost all the DMCd is converted into methylethylcadmium (MECd) and diethylcadmium (DECd). After mixing TMIn and TEGa at $x=0.3$, the main products are methyldiethylindium (MDEIn) and dimethylethylgallium (DMEGa). Conversely, at $x=0.7$, the three organoindium compounds exist in almost equal amounts, as do TMGa and TEGa .

For the group II sources, the overall equilibrium does not change significantly with increasing reactor temperature up to $200\text{ }^\circ\text{C}$. Above $200\text{ }^\circ\text{C}$, the DECd begins to

decompose, causing a shift in the reaction equilibrium towards the organozinc compounds. The reactivity of the group II compounds decreases in the following order: $\text{DECd} > \text{MECd} > \text{DMCd} > \text{DEZn} > \text{MEZn} > \text{DMZn}$. The shift towards more DMZn production at higher temperatures, and the high thermal stability of the MEZn and the DMZn, results in a low conversion of the organozinc compounds.

The changes of the partial pressures of the group III sources with temperature shows many similarities with those of the group II mixture. At 250 °C, the organoindium species start to decompose, while the concentration of TMGa increases. At 350 °C, the organoindium compounds and TEGa are depleted from the mixture, leaving the less reactive methylgallium species unconverted. Trimethylgallium does not decompose significantly below 500 °C.

There is a distinct difference in the uniformity of the $\text{Cd}_{1-y}\text{Zn}_y\text{Te}$ films grown at low and high x values. Figure 4 shows how the film composition and thickness change down the length of the reactor tube for x values of 0.4 and 0.9, and a growth temperature of 400 °C. For $x=0.4$, a fairly uniform film containing about 4% zinc is deposited throughout the heated zone. At the higher x value, a II-VI film containing almost pure CdTe is deposited at the inlet of the reactor, while a film of almost pure ZnTe is deposited at the end of the reactor. The film rich in CdTe at the inlet is almost four times as thick as the film rich in ZnTe near the outlet. The transition from cadmium- to zinc-rich film growth occurs at a point where all the cadmium containing species have been depleted from the gas phase. This point tends to shift towards the inlet with increasing growth temperature.

Grady et al. observed that ligand exchange reactions between trimethylamine alane and TMGa lead to compositional non-uniformity in AlGaAs MOVPE.⁷ Ligand exchange

reactions between the group III precursors were absent during operation at low pressure, resulting in high quality films.¹⁹ Our results presented above indicate that ligand exchange does occur between TMI_n and TEGa at low pressure. The InGaAs OMVPE experiments are in progress, and we foresee difficulties in depositing uniform films of In_{0.53}Ga_{0.47}As over the entire length of the susceptor. The more reactive ethylindium species produced by ligand exchange decompose at much lower temperatures than the less reactive methylgallium compounds. Depending on the growth temperature and composition of the feed gas, the large difference in reactivities of these sources may result in indium-rich films at the inlet, and gallium-rich films towards the outlet of the horizontal flow reactor. Reactors which minimize upstream mixing of the group II or group III precursors, and in which the gas contacts the entire wafer at once, such as in a vertical flow, rotating disc configuration, should be less susceptible to this problem.

CONCLUSIONS

Ligand exchange among the group II and among the group III precursors appears to be a general phenomenon in the growth of compound semiconductor alloys by OMVPE. Although these reactions are well documented in organometallic chemistry, their impact on the OMVPE process have not been widely recognized. The large difference in reactivities of the sources produced by ligand exchange makes it difficult to uniformly deposit the desired alloy composition over the entire area of a heated substrate in a horizontal flow reactor.

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Table 1. The relative partial pressures of the group II compounds in the reactor feed at two values of $x = \text{DEZn}/(\text{DEZn} + \text{DMCd})$.

x	Organometallic compounds					
	DMZn	MEZn	DEZn	DMCd	MECd	DECd
0.3	0.156	0.091	0.045	0.314	0.386	0.008
0.7	0.095	0.228	0.375	0.019	0.149	0.135

Table 2. The relative partial pressures of the group III compounds in the reactor feed at two values of $x = \text{TMIIn}/(\text{TMIIn} + \text{TEGa})$.

x	Organometallic compounds							
	TMGa	DMEGa	MDEGa	TEGa	TMIIn	DMEIn	MDEIn	TEIn
0.3	0	0.150	0.013	0.565	0.028	0.072	0.228	0
0.7	0.105	0.084	0.015	0.102	0.320	0.276	0.237	0

CAPTIONS TO FIGURES

Fig. 1. Infrared spectra between 850 and 450 cm^{-1} of (a) the group II organometallic compounds in the reactor feed during CdZnTe OMVPE at varying ratios of DMCd to DEZn, and (b) the group III organometallic compounds in the reactor feed during InGaAs OMVPE at varying ratios of TMIn to TEGa.

Fig. 2. Infrared spectra between 850 and 450 cm^{-1} of (a) the group II organometallic compounds present after mixing DMCd and DEZn, and (b) the group III organometallic compounds present after mixing TMIn and TEGa. All spectra are normalized to the same scale.

Fig. 3. The relative partial pressures of (a) DMCd and DEZn in the reactor feed during CdZnTe OMVPE, and (b) TMIn and TEGa in the reactor feed during InGaAs OMVPE, at varying x values.

Fig. 4. The dependence of the film composition (a) and thickness (b) on the relative axial position in the reactor during CdZnTe OMVPE with DMCd, DEZn and DIPTe at 400 °C, a II/VI ratio of 1.0, and x values of 0.4 and 0.9.

Figure 1

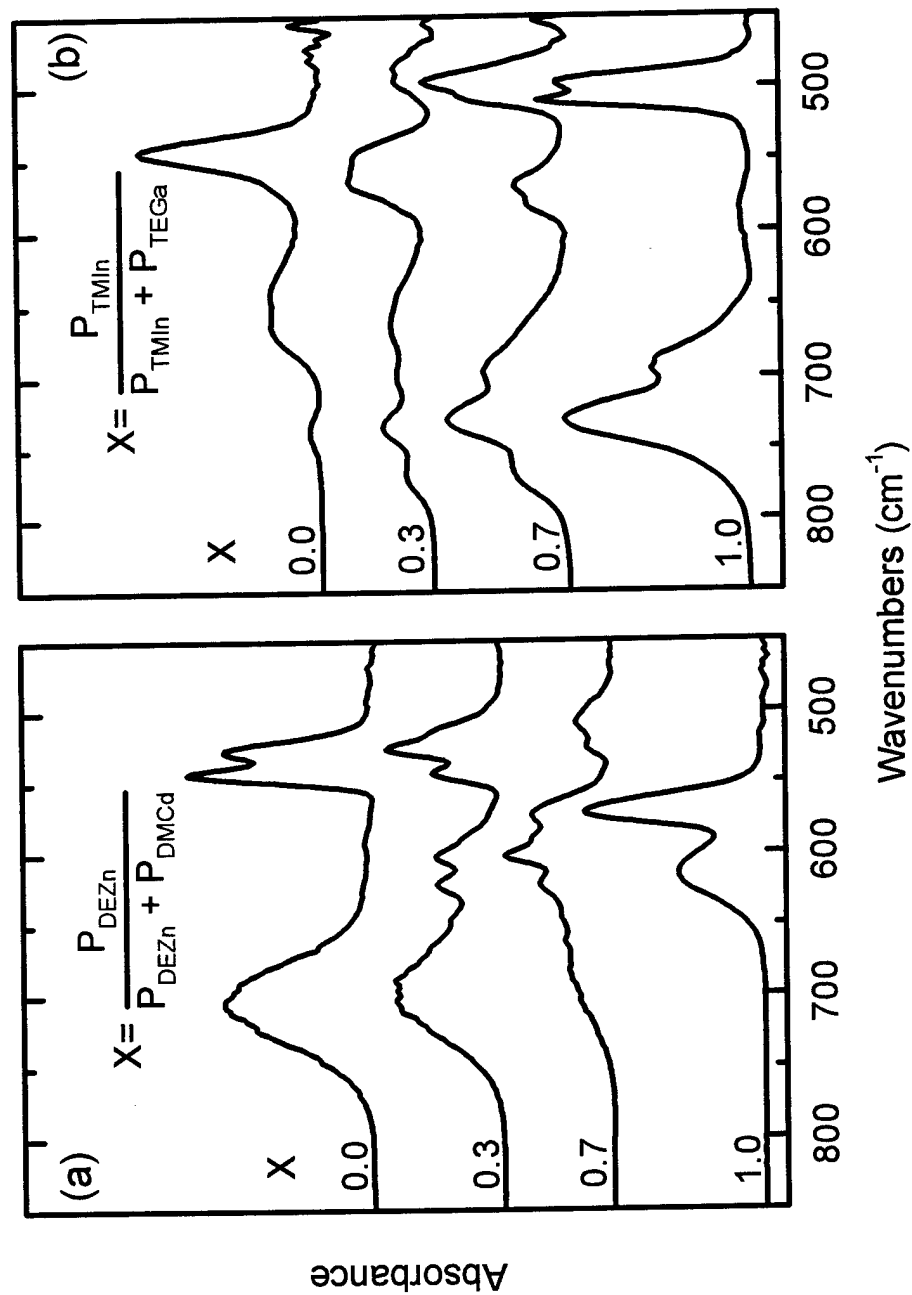


Figure 2

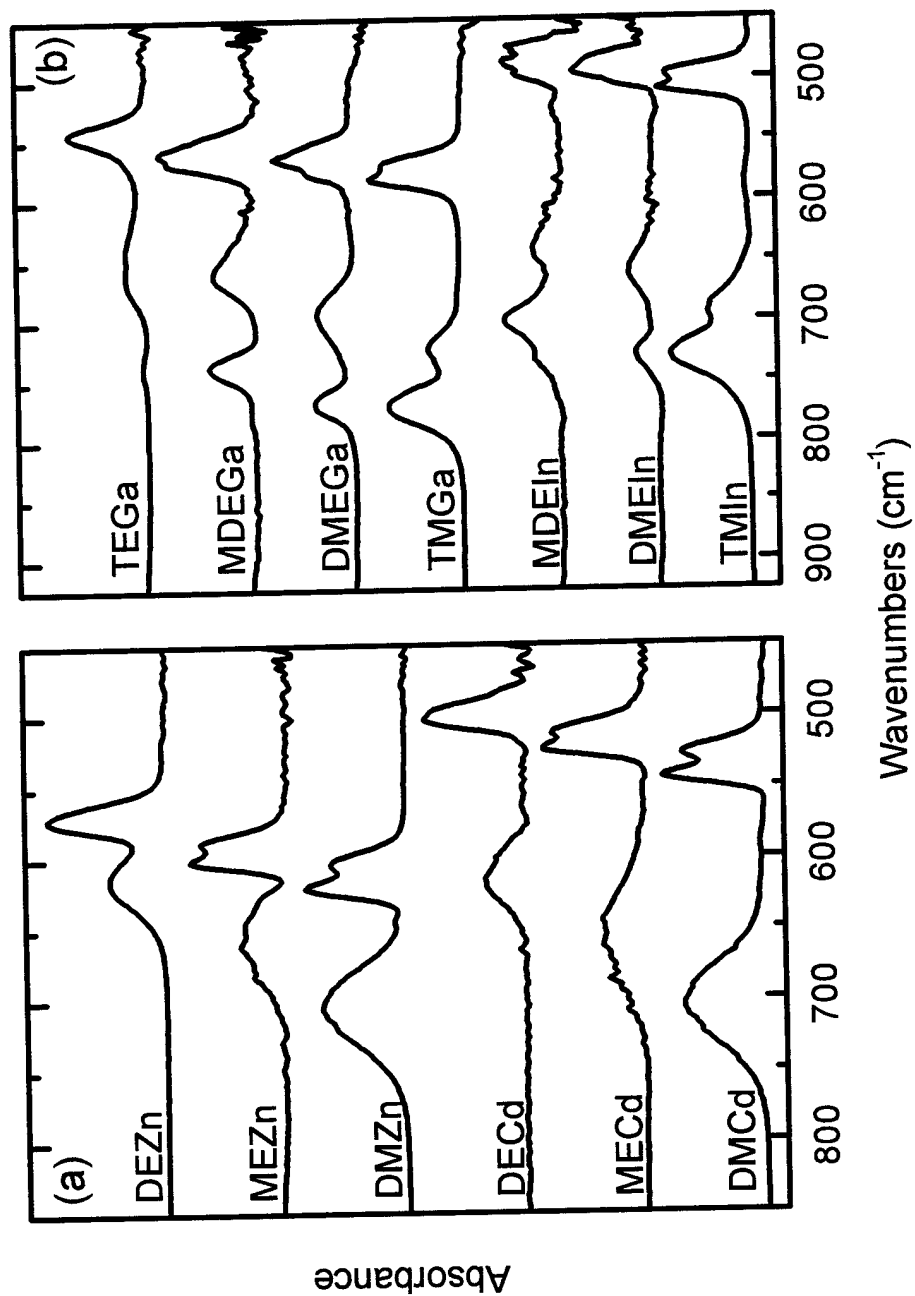
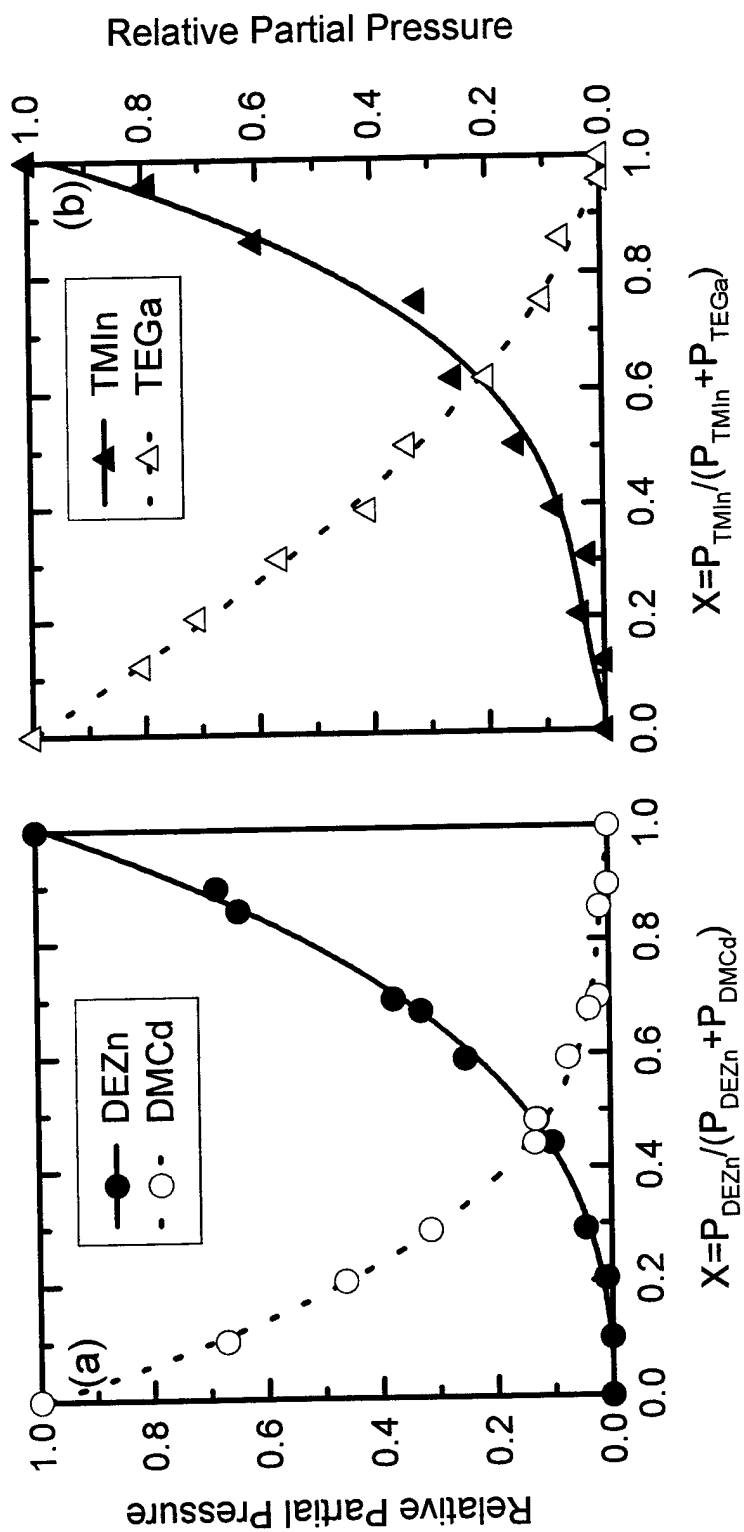


Figure 3



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Figure 4

